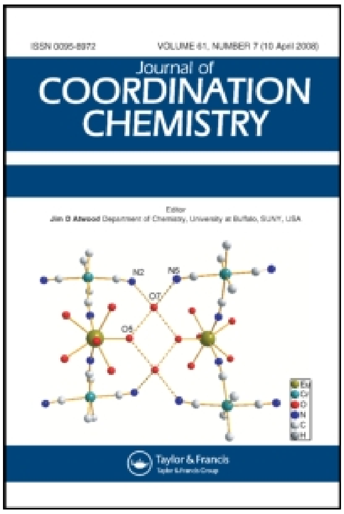

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# PROTONATED LIGAND OUTER-SPHERE COMPLEX FORMED IN THE REACTION OF 6-METHYLPYRIDINE-2-CARBOXALDEHYDE PHENYLHYDRAZONE WITH $Ph_2SnCl_2$. A TRUE CASE OF HYDROGEN BONDING INVOLVING AN Sn–Cl BOND

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The reaction of 6-methylpyridine-2-carboxaldehyde phenylhydrazone (L) with $Ph_2SnCl_2$ has resulted in the formation of a complex salt $[LH^+]_2[Ph_2SnCl_4]^{2-}$. X-ray diffraction studies on the salt reveal the structure of the $[Ph_2SnCl_4]$ dianion to be centrosymmetric with the tin atom in a distorted octahedral *trans*-$C_2Cl_4$ environment; Sn–Cl(1) 2.598(2), Sn–Cl(2) 2.5875(7) and Sn–C(1) 2.146(3) Å. Associated with the dianion are two $[PhN(H)NC(H)C_5H_3(Me)N(H)]$ cations *via* two hydrogen bonding contacts apiece, unusually involving a true Sn–Cl bond.

*Keywords:* Complex salt; 6-methylpyridine-2-carboxaldehyde phenylhydrazone; hydrogen bonding; Sn–Cl bond

## INTRODUCTION

Schiff base ligands derived from the condensation of pyridine-2-carboxaldehyde and its substituted analogues with various amines have been known to coordinate to transition metals *via* the pyridyl nitrogen atom and

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the aminic or iminic nitrogen.[1,2] Mandal[3] showed that pyridine-2-carboxaldehyde phenylhydrazone displays bidentate chelation and unidentate modes of bonding towards ($\eta^5$-cyclopentadienyl)ruthenium(II) complexes and recently there have been reports regarding the tin complexes of several aroylhydrazones, which exhibit a tendency to produce stereochemistries with high coordination numbers.[4-6] The present work reports the reaction of 6-methylpyridine-2-carboxaldehyde phenylhydrazone, **L**, with $Ph_2SnCl_2$ which leads to the unprecedented formation of a protonated ligand outer-sphere complex, $[LH^+]_2[Ph_2SnCl_4]^{2-}$. An X-ray structural investigation of the complex has been performed and the results, along with other physical data, are presented and discussed herein.

## EXPERIMENTAL

### Reagents

6-Methylpyridine-2-carboxaldehyde and $Ph_2SnCl_2$ were purchased from Aldrich Chemical Company, while phenylhydrazine was supplied by Fluka Chemie AG.

### Synthesis of 6-Methylpyridine-2-carboxaldehyde phenylhydrazone (L)

The ligand **L** was prepared by the dropwise addition of a 10 cm$^3$ of a dry ethanolic solution of phenylhydrazine (1.08 g, 10 mmol) to an ethanolic solution of 6-methylpyridine-2-carboxaldehyde (1.22 g, 10 mmol). The reaction mixture was stirred for 2 h whereupon the yellowish crystals that separated were filtered and recrystallized, from ethanol. Yield, 1.60 g (75%); m.p. 194–196°C. *Anal.*: Calcd. for $C_{13}H_{13}N_3$(%): C, 73.91; H, 6.20; N, 19.89. Found: C, 73.08; H, 6.23; N, 19.54. IR (KBr): $\nu$, 3213 (N–H), 1604 (C=N) cm$^{-1}$; NMR ($^1$H, $CDCl_3$): $\delta$, 2.65 (s, $CH_3$); 6.90–8.09 (m, aromatic); 7.91 (s, HC=N); 8.69 (s, NH) ppm. NMR ($^1$H, DMSO-$d^6$): $\delta$, 2.46 (s, $CH_3$); 6.77–7.88 (m, aromatic); 7.84 (s, HC=N); 10.62 (s, NH) ppm.

### Synthesis of Bis[6-methylpyridine-2-carboxaldehyde hydrazonium]-dichlorodiphenylstannate(IV), $[Ph_2SnCl_4][PhN(H)NC(H)C_5H_3(Me)N(H)]_2$, $[LH^+]_2[Ph_2SnCl_4]^{2-}$

A solution of diphenyltin dichloride (0.81 g, 3 mmol) in 10 cm$^3$ of dry dichloromethane was added to 6-methylpyridine-2-carboxaldehyde phenylhydrazone (1.26 g, 6 mmol) in 20 cm$^3$ of the same solvent. The reaction mixture was stirred for 2 h and was then left standing at room temperature for a day whereupon yellow crystals were obtained. The product was then recrystallized from dry ethanol. Yield, 2.12 g (84%); m.p. 198–200°C. *Anal.*: Calcd. for $C_{38}H_{38}Cl_4N_6Sn$(%): C, 54.37; H, 4.56; N, 10.01; Sn, 14.14. Found: C, 54.22; H, 4.23; N, 9.89; Sn, 14.04. IR (KBr): $\nu$, 3275 (N–H); 1640 (C=N) cm$^{-1}$; NMR ($^1$H, $CDCl_3$): $\delta$, 2.63 (s, $CH_3$); 7.20–7.74 (m, aromatic); 7.73 (s, HC=N); 7.74 (s, NH) ppm. NMR ($^1$H, DMSO-$d^6$): $\delta$, 2.46 (s, $CH_3$); 6.80–7.92 (m, aromatic); 7.92 (s, HC=N); 10.63 (s, NH) ppm.

### Characterization of Compounds

Carbon, hydrogen and nitrogen analyses were carried out on a Control Equipment Corporation 240 XA instrument at the School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia. The tin analysis was performed using an Instrumental Laboratory 357 atomic absorption spectrophotometer. IR data of the ligand and the complex were recorded using a Perkin Elmer FTIR infrared spectrophotometer in the frequency range 4000–450 cm$^{-1}$. Samples were prepared as KBr discs. $^1$H NMR spectra were recorded on a Brüker AC-P 300 MHz NMR spectrometer using both $CDCl_3$ and DMSO-$d^6$ as solvents with TMS as the internal standard.

### Determination of the Crystal Structure of $[LH^+]_2[Ph_2SnCl_4]^{2-}$

Intensity data for an yellow crystal (0.16 × 0.16 × 0.32 mm) were measured at room temperature on a Rigaku AFC6R diffractometer fitted with Mo-K$\alpha$ radiation (graphite monochromator, $\lambda = 0.71073$ Å) using the $\omega : 2\theta$ scan technique such that $\theta_{max}$ was 27.5°. No decomposition of the crystal occurred during the data collection. The data set was corrected for Lorentz and polarization effects[7] and for absorption employing an empirical procedure;[8] maximum and minimum transmission factors: 1.000 and 0.911. Of the 4771 data collected, 4550 were unique and of these 3318 satisfied the $I \geq 3.0\sigma(I)$ criterion of observability and were used in the subsequent analysis.

The structure was solved by direct methods[9] and refined by a full-matrix least-squares procedure based on $F$.[7] The non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were included in the model in their calculated position except for the nitrogen-bound hydrogen atoms which were located from a difference map. Refinement was continued with sigma weights $1/\sigma^2(F)$ to $R = 0.029$ and $R_w = 0.033$; the maximum residual electron density peak in the final difference map was 0.63 e Å$^{-3}$. Crystal data and refinement parameters are summarized in Table I. Final fractional atomic coordinates for the non-hydrogen atoms are listed in Table II and selected interatomic distances and angles are given in Table III. The crystallographic numbering scheme employed is shown in Figure 1 which was drawn using ORTEP.[10] Data manipulations were performed with

TABLE I Crystallographic data and details of structure refinement for $[LH^+]_2[Ph_2SnCl_4]^{2-}$

| | |
|---|---|
| Formula | $C_{38}H_{38}Cl_4N_6Sn$ |
| Formula weight | 837.3 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| $a$ (Å) | 11.253(8) |
| $b$ (Å) | 15.527(9) |
| $c$ (Å) | 11.482(5) |
| $\beta$ (°) | 108.56(4) |
| $V$ (Å$^3$) | 1901(1) |
| $Z$ | 2 |
| $D_{expt}$ (g cm$^{-3}$) | 1.465 |
| $F$(000) | 852 |
| $\mu$ (cm$^{-1}$) | 9.88 |
| $R$ | 0.029 |
| $R_w$ | 0.033 |

TABLE II Fractional atomic coordinates for the non-hydrogen atoms in $[LH^+]_2[Ph_2SnCl_4]^{2-}$

| *Atom* | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Sn[a] | 0 | 1/2 | 0 |
| Cl(1) | 0.21037(6) | 0.41617(5) | 0.07709(7) |
| Cl(2) | 0.02317(7) | 0.51861(5) | −0.21568(7) |
| N(1) | 0.4599(2) | 0.5450(2) | 0.1468(2) |
| N(2) | 0.4598(2) | 0.5924(2) | 0.0493(2) |
| N(3) | 0.2391(2) | 0.6396(2) | −0.2405(2) |
| C(1) | 0.0981(2) | 0.6186(2) | 0.0608(2) |
| C(2) | 0.1874(3) | 0.6249(2) | 0.1757(3) |
| C(3) | 0.2506(3) | 0.7022(2) | 0.2142(3) |
| C(4) | 0.2257(4) | 0.7723(2) | 0.1372(4) |
| C(5) | 0.1362(4) | 0.7672(2) | 0.0233(4) |
| C(6) | 0.0727(3) | 0.6905(2) | −0.0156(3) |
| C(7) | 0.5638(3) | 0.5421(2) | 0.2519(3) |
| C(8) | 0.5543(3) | 0.4953(2) | 0.3518(3) |
| C(9) | 0.6570(4) | 0.4895(2) | 0.4576(3) |
| C(10) | 0.7676(4) | 0.5298(3) | 0.4640(3) |
| C(11) | 0.7769(3) | 0.5759(2) | 0.3646(3) |
| C(12) | 0.6759(3) | 0.5820(2) | 0.2580(3) |
| C(13) | 0.3594(3) | 0.5884(2) | −0.0448(3) |
| C(14) | 0.3521(3) | 0.6380(2) | −0.1531(3) |
| C(15) | 0.2135(3) | 0.6833(2) | −0.3474(3) |
| C(16) | 0.3075(4) | 0.7310(2) | −0.3681(3) |
| C(17) | 0.4245(4) | 0.7307(2) | −0.2811(3) |
| C(18) | 0.4497(3) | 0.6835(2) | −0.1746(3) |
| C(19) | 0.0833(4) | 0.6757(3) | −0.4338(4) |

[a] Atom located at centre of inversion.

TABLE III Selected interatomic distances (Å) and angles (°) for $[LH^+]_2[Ph_2SnCl_4]^{2-}$

| | | | |
|---|---|---|---|
| Sn–Cl(1) | 2.598(2) | Sn–Cl(2) | 2.5875(7) |
| Sn–C(1) | 2.146(3) | N(1)–N(2) | 1.340(3) |
| N(1)–C(7) | 1.388(4) | N(2)–C(13) | 1.293(3) |
| N(3)–C(14) | 1.346(4) | N(3)–C(15) | 1.351(4) |
| C(13)–C(14) | 1.444(4) | | |
| Cl(1)–Sn–Cl(2) | 91.35(4) | Cl(1)–Sn–Cl(2)[a] | 88.65(4) |
| Cl(1)–Sn–C(1) | 90.03(8) | Cl(1)–Sn–C(1) | 89.97(8) |
| Cl(2)–Sn–C(1) | 91.02(8) | Cl(2)–Sn–C(1) | 88.98(8) |
| Sn–C(1)–C(2) | 120.9(2) | Sn–C(1)–C(6) | 120.1(2) |
| N(2)–N(1)–C(7) | 121.3(2) | N(1)–N(2)–C(13) | 116.1(2) |
| C(14)–N(3)–C(15) | 124.3(3) | N(2)–C(13)–C(14) | 119.3(3) |
| N(3)–C(14)–C(13) | 115.6(3) | | |

[a] Primed atoms are related by a crystallographic centre of inversion.

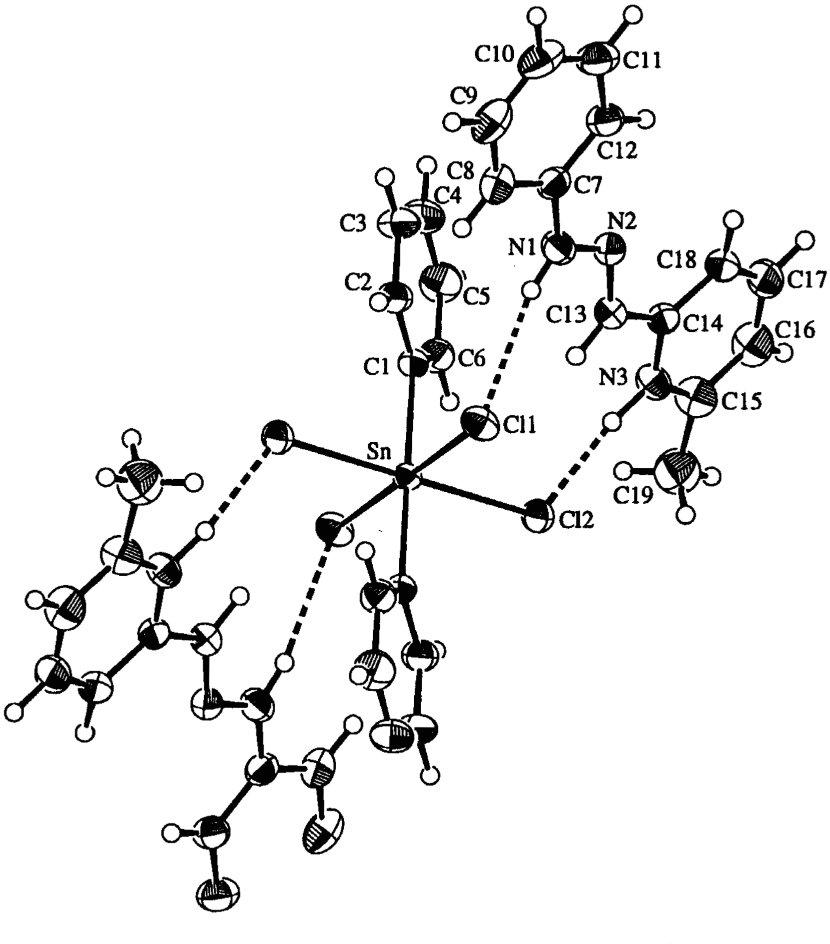

FIGURE 1 Molecular structure and crystallographic numbering scheme for $[LH^+]_2[Ph_2SnCl_4]^{2-}$; hydrogen bonding is indicated by dashed lines.

the teXsan program installed on an Iris Indigo work station. Lists of atomic coordinates, thermal parameter and observed and calculated structure factors are available on request from the authors.

## RESULTS AND DISCUSSION

In contrast to other hydrazones which coordinate to metals through various coordination sites,[3–6,11–13] 6-methylpyridine-2-carboxaldehyde phenylhydrazone reacts with $Ph_2SnCl_2$ to give an outer-sphere tin complex. The molecular structure of the complex salt is illustrated in Figure 1 and selected interatomic parameters are listed in Table III. The unit cell in the crystal features two $[Ph_2SnCl_4]$ dianions, each of which is situated on a crystallographic centre of inversion and four $[PhN(H)N(C)C_5H_3(Me)N(H)]$ cations.

The tin atom in the central dinegatively charged moiety exists in an essentially *trans*-$C_2Cl_4$ donor set; the greatest deviation from ideal octahedral geometry is found in the Cl(1)–Sn–Cl(2) angle of 91.35(4)°. The two independent Sn–Cl distances of 2.598(2) and 2.5875(7) Å are equal within the $4\sigma$ level and the Sn–C(1) separation is 2.146(3) Å.

Counterbalancing the anionic group are two $[PhN(H)NC(H)C_5H_3(Me)N(H)]$ cations, each of which is protonated at the pyridine nitrogen atom; both of the nitrogen-bound hydrogen atoms were located in a difference map. Such a mode of protonation is unusual for complex salts involving Schiff base ligands, which are normally protonated at the imine nitrogen atom.[14–16] In the present complex, the iminic nitrogen (N2) is unprotonated. Confirmation of the presence of hydrogen at each of N(1) and N(3) atoms is found in the nature of the intermolecular contacts in the structure. The two $[PhN(H)NC(H)C_5H_3(Me)N(H)]$ cations are associated with the dianion *via* hydrogen bonding contacts involving the nitrogen-bound atoms and the tin-bound chloride atoms as shown by the dashed lines in Figure 1. The occurrence of true hydrogen bonding interactions as described above is indicated by the significant elongation of the Sn–Cl bond distances (*cf* 2.30–2.48 Å for normal Sn–Cl bonds[17]) in the present complex.

An earlier report of such bonding in the complex salt $[(C_8H_8NS)^+]_2[(C_4H_9Sn(OH)Cl_3)_2]^{2-}2[C_8H_7NS]$[18] has been disputed by a reinvestigation of the crystal structure of the complex[19] whilst the rather long H···Cl(Sn) distances of ~2.90 Å found in $[Cl_3(H_2O)Sn\text{–}OH\text{–}]_2 \cdot 4H_2O$[20] can at best be considered as very weak interactions and is not indicative of true hydrogen bonding. The N(1)–H···Cl(1) separation is 2.48 Å and the angle subtended at the H(1*n*) atom is 168.0° [Cl(1)···N(1) is 3.331(3) Å] and for the

N(3)–H···Cl(2) contact, the separation is 2.14 Å and the angle is 172.2° [Cl(2)···N(3) is 3.155(3) Å]. Within the cation, the N(1)–N(2) and N(2)–C(13) bond distances of 1.340(3) and 1.293(3) Å, respectively, are consistent with the presence of a single and double bond, respectively, about the N(2) atom. That the cation is essentially planar is seen in the values of the C(8)/C(7)/N(1)/N(2), N(1)/N(2)/C(13)/C(14) and N(2)/C(13)/C(14)/N(3) torsion angles of 176.5(3), 179.7(3) and −171.4(3)°, respectively.

The microanalytical data are in accordance with the formulation $[LH^+]_2[Ph_2SnCl_4]^{2-}$. Inspection of IR data shows that the band at 1604 $cm^{-1}$ due to the C=N stretching vibration in the uncoordinated ligand is shifted to 1640 $cm^{-1}$ upon complexation.[21] A preliminary investigation shows[22] that the reaction of 6-methylpyridine-2-carboxaldehyde phenylhydrazone with dimethyltin(IV) dichloride and *n*-butyltin(IV) trichloride respectively also leads to the formation of similar complex salts.

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